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Silylation–desilylation of propargyl amides: rapid synthesis of functionalised aldehydes and β-lactams

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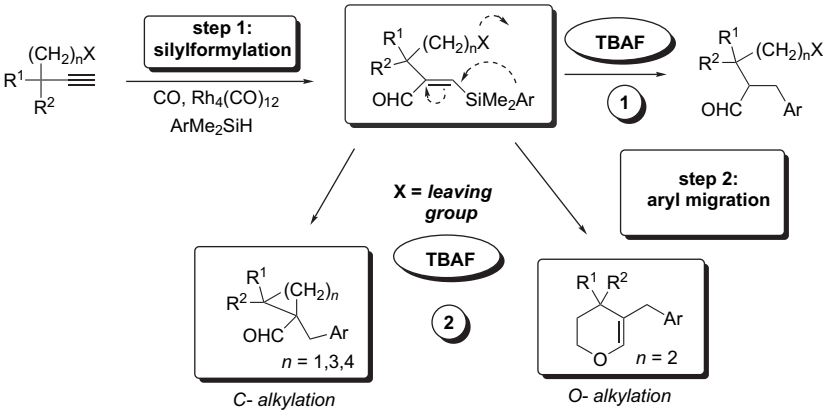
Abstract—Propargyl functionalised β-silylalkenals were easily prepared starting from suitable propargyl compounds by a silylformylation process. In particular the use of propargyl tosyl amides allowed the synthesis of α,β-unsaturated aldehydes through a two-step sequence of silylformylation–desilylation reactions. TBAF was employed to induce the desilylation process that was performed under very mild experimental conditions and occurred along with an elimination step of the tosylamido moiety affording 2-methylaryl-2-alkenals with good yields and stereoselectivity. When the tosyl amides were reacted with a hydrosilane in the presence of catalytic amounts of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) α-silylmethylene-β-lactams were synthesised through a silylcarbocyclisation process. A high chemoselectivity towards the β-lactam was observed when dialkyl propargyl amides were employed. The obtained β-lactams were easily transformed into the corresponding methylaryl-β-lactams by fluoride induced aryl migration–desilylation with total retention of configuration of the migrating group and complete stereoselectivity towards the more stable β-lactam (*E*)-isomer.

1. Introduction

Although catalytic hydrosilylation[1] reactions are well known processes of industrial importance, in the last two decades other reactions of silicon compounds promoted by transition metal complexes have been revealed and intensively developed.[2] They include double silylation, dehydrogenative coupling of hydrosilanes, coupling of olefins with hydrosilanes and with vinylsilanes, metathesis of silicon containing olefins, silylcarbonylation and silylformylation reactions. In the last case, treatment of terminal acetylenes with CO and a hydrosilane usually results in the formylation of the internal sp carbon of the triple bond and in the addition of the silicon group to the terminal one, thus affording (*Z*)-β-silylalkenals in high yields and with high degree of regio and stereochemical control (Scheme 1, step 1).[3]



Scheme 1.

Keywords: Silylformylation; Silylcarbocyclisation; Desilylation; α,β-Unsaturated aldehydes; β-Lactams.
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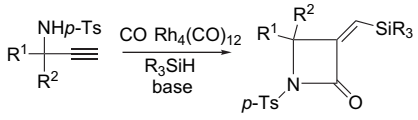
The silylformylation reaction has been studied extensively in the past few years since it can be easily extended to unsaturated compounds bearing several functional groups such as alcohols, ethers, esters, ketones, aldehydes, halogens and double bonds. Moreover, β-silylalkenals can be easily transformed into silyl substituted dienes,[4] dienones,[5] α,β-unsaturated ketones,[6] and can be important precursors for the synthesis of more complicated molecules via Peterson olefination,[7] Nazarov type cyclopentenone annulation,[8] Trost type cyclopentane annulation,[9] isomerisation of the double bond, reduction and Wittig transformation of the carbonyl group.[10]

Recently[11] we observed that β-arylsilylalkenals can be reacted with tetrabutylammonium fluoride (TBAF) affording 2-methylaryl aldehydes in good yield. The reaction involved the fluoride promoted 1,2-migration of the aryl group of the silyl moiety to the adjacent carbon atom followed by a desilylation step (Scheme 1, step 2). CN, OH or unsaturated functionalities (C=C, C≡C) in the ω position of the alkyne precursor were not involved in the migration step but were directly transferred to the saturated products (Scheme 1, step 2, route 1).[12] On the contrary, when a leaving group, such as a halide or a tosyl substituent, was situated at the end of the hydrocarbon chain, ring closure reactions took place with the formation of three-, five- and six-membered ring products. Cycloalkanecarbaldehydes and 5-methylaryl-3,4-dihydro-2*H*-pyrans were generated by intramolecular C-alkylation or O-alkylation of the carbanion formed after the fluoride addition to the silicon atom and subsequent aryl migration (Scheme 1, step 2, route 2).[12]

In this paper we initially present an extension of our silylation–fluoride promoted aryl migration protocol to several acetylenes characterised by substituents in the propargylic position.[13] Particular attention will be paid to propargyl amides since they are useful synthetic building blocks that can be precursors of biologically important molecules such as β-lactams. Indeed Matsuda reported a direct synthesis of β-lactam rings starting from propargyl amides through a one pot base catalysed silylcarbocyclisation that requires a sterically hindered hydrosilane such as $^{t}BuMe_2SiH$ to succeed (Scheme 2).[14]



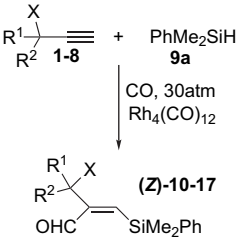
Scheme 2.

It is well known that the β-lactam skeleton is the key structural unit of the most widely employed β-lactam antibiotics and inhibitors of β-lactamase[15] and can be an important intermediate for the synthesis of α- and β-amino acids, aspartic acid derivatives, alkaloids, heterocycles and taxoids.[16] Hence we took into account the application of the silylcarbocyclisation reaction to suitable propargyl amides and aryldimethylsilanes that could allow the formation of 3-(arylsilylmethylene)-β-lactams. In particular, a detailed study of the reactivity of different arylsilanes is reported and the application of the TBAF induced aryl migration–desilylation step to the synthesis of functionalised β-lactams is investigated.

2. Results and discussion

Initially the silylformylation reaction of propargyl compounds **1**–**8** was considered and the principal results obtained are described in Scheme 3 and summarised in Table 1. The reactions were performed in a stainless steel autoclave, under 30 atm of CO, in the presence of catalytic amounts of $Rh_4(CO)_{12}$ (0.1–0.5 mol % with respect to the acetylene) at 100 °C. These preliminary data confirmed that the nature of the propargylic substituents is a key element of the process. Indeed, 3-bromopropyne **1** and sulfonates **3** and **4** were completely consumed during the reaction but the formation of unidentified decomposed material was observed (Table 1, entries 1, 3 and 4). The propargyl alcohol **2**, the benzoate **5** and acetate **6** were successfully converted into the corresponding β-silylalkenals (*Z*)-**11**, **14** and **15** (Table 1, entries 2, 5 and 6). As far as the propargyl amides **7** and **8a** are concerned, both *tert*-butoxy carbonyl (Boc) and tosyl protections of the nitrogen atom were effective for the formation of the functionalised aldehydes (*Z*)-**16** and (*Z*)-**17** (Table 1, entries 7 and 8). In particular the reaction of the propargyl tosyl amide was quantitative affording the expected product in high yield (71% of pure compound).

Considering our interest in the propargyl amides as precursors of more complex compounds such as β-lactams we extended our investigations to the reactivity of tosyl amides and arylsilanes with different steric and electronic requirements (Scheme 4). As can be easily deduced from the data described in Table 2 (step 1), the silylformylation of propargyl amides was appreciably affected by the structure of the acetylenic reagents, in agreement with the results



Scheme 3.

Table 1. Silylformylation of propargyl derivatives **1**–**8a** with dimethylphenylsilane **9a**[a]

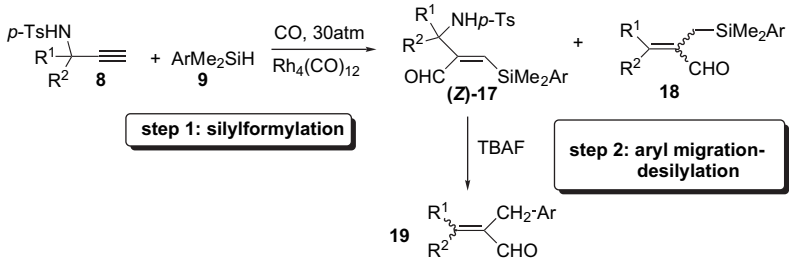
Entry	Substrate	X	R^1	R^2	Yield[b] (%)	
1	**1**	Br	H	H	(*Z*)-**10**	dec
2	**2**	OH	H	H	(*Z*)-**11**	83[c] (71)
3	**3**	OSO_2Me	H	H	(*Z*)-**12**	dec
4	**4**	OSO_2Ph	H	H	(*Z*)-**13**	dec[d]
5	**5**	OCOPh	Me	H	(*Z*)-**14**	78 (54)
6	**6**	OCOMe	Me	Et	(*Z*)-**15**	100 (75)
7	**7**	NHBoc	Me	Et	(*Z*)-**16**	70 (63)
8	**8a**	NH-*p*-Ts	Me	H	(*Z*)-**17**	91 (71)

[a] Reactions were carried out with 2 mmol of silane, 2 mmol of propargyl substrate, 2×10^{-3}–10^{-2} mmol of $Rh_4(CO)_{12}$, 3 mL of CH_2Cl_2 in a stainless steel autoclave under 30 atm of CO at 100 °C for 24 h.

[b] Determined by GLC of the reaction mixture after work up. The isolated yields of pure compounds are reported in parentheses.

[c] Reaction performed at room temperature; 17% of (*E*)-isomer was detected by ^1H NMR analysis.

[d] When the reaction was performed at room temperature the propargyl precursor was recovered unreacted.



Scheme 4.

Table 2. Silylformylation–desilylation reactions of propargyl amides **8**

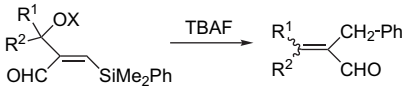
Entry	**8**	R^1	R^2	**9**	Ar	Step 1: silylformylation[a]				Step 2: aryl migration[b]	
						Conv.[c] (%)	(*Z*)-**17**, **18**[d]	Yield[c] (%)		**19**	Yield[e] (%) (*E*/*Z*)[f]
								(*Z*)-**17**	**18**[d]		
1	**a**	H	Me	**a**	Ph	100	**aa**	91 (71)[g]	—	**aa**	52 (100/0)
2	**b**	H	^{t}Bu	**a**	Ph	73	**ba**	95 (49)[g]	—	**ba**	45 (100/0)
3	**c**	Me	Me	**a**	Ph	100	**ca**	87 (42)	13	**ca**	75
4	**d**	Me	Et	**a**	Ph	79	**da**	80 (44)	20	**da**	59 (65/35)
5	**e**	Me	^{t}Bu	**a**	Ph	53	**ea**	38 (15)[h]	—	—	—
6	**a**	H	Me	**b**	*o*-Me–C_6H_4	65	**ab**	100 (38)	—	**ab**	67 (100/0)
7	**c**	Me	Me	**c**	*p*-OMe–C_6H_4–	68	**cc**	87 (48)	13	**cc**	55

[a] Reactions were performed with 2 mmol of silane, 2 mmol of amide, 2×10^{-3}–10^{-2} mmol of $Rh_4(CO)_{12}$, 3 mL of CH_2Cl_2 in a stainless steel autoclave under 30 atm of CO at 100 °C for 24 h.
[b] Reactions were performed by adding 1 mmol of β-silylalkenals to a THF solution (10 mL) of TBAF (2.5 mmol) at room temperature; 100% conversion of the precursors was detected by ^{1}H NMR analyses.
[c] Determined by GLC of the reaction mixture after work up. The isolated yields of pure compounds are reported in parentheses.
[d] An *E*/*Z* mixture was always observed.
[e] Yields of pure compounds.
[f] Diastereomeric ratio was obtained by ^{1}H NMR analysis. *E* and *Z* configurations of the products were determined by NOE experiments.
[g] Small amounts of isomerisation byproducts were observed.
[h] Hydrosilylated products (62%) were detected by ^{1}H NMR analysis.

previously observed studying the reaction of nonfunctionalised 1-alkynes.[10] Indeed, the less hindered tosyl amides reacted rapidly with almost total selectivity towards the corresponding β-silylalkenals (*Z*)-**17** (Table 2, step 1, entries 1 and 2). On the other hand, decreases in both the reaction rate and selectivity were detected when the silylformylation was carried out on acetylenes with bulky substituents on the propargyl carbon (Table 2, step 1, entries 3–5). In particular, in the case of *N*-(1-*tert*-butyl-1-methyl-2-propynyl)-*p*-toluenesulfonamide **8e** (Table 2, entry 5), the conversion after 24 h was only 53% and the hydrosilylation reaction was highly competitive with the formylation one (62% vs 38%). An analogous reaction trend was observed when hindered arylsilanes were employed: the use of *ortho*-tolyldimethylsilane resulted in a significant lowering of the reaction rate with respect to Me_2PhSiH (Table 2, entry 6 vs entry 1). However, the chemoselectivity of the process was quite good, thus allowing the extension of the silylformylation of propargyl amides to functionalised hydrosilanes.

The obtained β-silylalkenals (*Z*)-**17** were then submitted to the aryl migration–desilylation process (Scheme 4, Table 2, step 2). The reactions were performed under very mild experimental conditions, adding 1 mmol of aldehyde to a THF solution of TBAF (2.5 mmol) and hydrolysing immediately with water. Complete consumption of the reagents was observed and the products were recovered in good yields. In this case, the 1,2-anionotropic rearrangement is coupled with an elimination step of the tosyl amide moiety yielding 2-methylaryl-2-alkenals **19**. The reaction was totally stereoselective when a tertiary allylic carbon was present on the (*Z*)-**17** precursors and the more stable isomer (*E*) was exclusively formed (Table 2, step 2, entries 1, 2 and 6). The 1,2-rearrangement of the aromatic ring occurred with complete retention of the original configuration of the Ar, as observed in the cases of *ortho*- and *para*-functionalised phenyl silanes (Table 2, step 2, entries 6 and 7).

The described silylformylation–desilylation protocol represents a new simple pathway for the synthesis of α,β-unsaturated aldehydes from propargyl tosyl amides. An improvement of this methodology was achieved by replacing the amide moiety on the acetylene precursors with a benzoate or an acetate group. The propargyl esters can be generally prepared by means of easy organic chemistry procedures[17] starting from the corresponding alcohols (often commercially available) thus enhancing the applicability of the protocol. Indeed, α,β-unsaturated aldehydes **19aa** and **19da** were quantitatively generated by the TBAF induced reactions of β-silylalkenals (*Z*)-**14** and (*Z*)-**15** derived from propargyl benzoate and propargyl acetate **5** and **6**, respectively (Scheme 5). As shown in Scheme 5 the presence of a good leaving group induced the elimination step that occurred with complete selectivity towards the (*E*)-isomer in the case of benzoate (*Z*)-**14** confirming the stereochemical trend described in Table 2.



	R1	R2	X	n	yield	E/Z
(Z)-14	Me	H	COPh	(Z)-19aa	69%	100/0
(Z)-15	Me	Et	COMe	(Z)-19da	75%	57/43

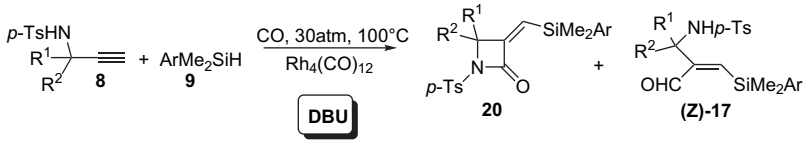
Scheme 5.

The good results obtained both in the silylformylation and in the desilylation processes of the tosyl amides prompted us to explore the reactivity of such substrates in the preparation of functionalised β-lactams through the silylcarbocyclisation–desilylation sequence. Initially we investigated the reactivity of *N*-(1-*tert*-butyl-2-propynyl)-*p*-toluene sulfonamide **8b** (Scheme 6, Table 3, entries 1–3) chosen as a model substrate. The reactions were performed with equimolar amounts of silane and amide and catalytic quantities both of $Rh_4(CO)_{12}$ (0.1 mol %) and of DBU (10%). The silylformylation process was highly competitive with the silylcarbocyclisation reaction. Only in the presence of a sterically hindered hydrosilane such as *ortho*-tolyldimethylsilane (Table 3, entry 3) a good amount of the desired β-lactam was formed, but the reaction rate was quite slow (59% of conversion after 4 h).

This reaction trend completely changed when amides with a quaternary α-carbon atom were employed. Indeed a high chemoselectivity towards the β-lactam was observed when dialkyl functionalised propargyl amides were reacted (Table 3, entries 4–9) regardless of the steric requirements of the hydrosilanes. The use of functionalised silanes allowed the preparation of the polyfunctionalised β-lactams **20ee–eg**. It is noteworthy that the reaction with dimethylthiophenylsilane **9g** determined the addition of the heteroaromatic ring on the silylmethylene portion of the product **20eg**. The obtained results clearly indicated that the structure of the propargyl precursors played a crucial role in the selectivity of the reaction, the presence of a bulky propargyl carbon being essential to force the closure of the ring (cf. entries 1–3 vs entries 4–9, Table 3). Moreover the high acidity of the NH-tosyl proton seemed to be fundamental for the β-lactam formation since the cyclisation process requires the removal of the nitrogen proton by the base DBU.

This hypothesis was confirmed by the results obtained reacting different arylsilanes with 3-amino-3-methyl-1-pentyne protected by a benzyl (**21**) or a *tert*-butoxy carbonyl group (**7**) (Scheme 7, Table 4). It is evident from the data reported in Table 4 that both the presence of a Boc and a CH_2Ph functionality on the nitrogen atom clearly favoured the silylformylation reaction that occurs without breaking of the N–H bond (Table 4, entries 1 and 2); even the use of 1 equiv of the base was ineffective to afford the β-lactam ring (Table 4, entry 3). In the case of the benzyl derivative **21** the β-silylalkenal could not be isolated since it immediately rearranged to the elimination product **18** (Table 4, entries 2 and 4).[13,18] When different arylsilanes were tested, only $MePh_2SiH$ showed 54% chemoselectivity towards the silylcarbocyclisation process (Table 4, entry 4), while no reaction was detected employing more hindered silanes such as triphenylsilane **9i** or *ortho*-tolyldimethylsilane **9b** (Table 4, entries 5 and 6).

With the access to the arylmethylene β-lactams **20** in hand we turned to the TBAF promoted aryl migration–desilylation process that would allow a very easy and direct synthesis of 3-methylaryl-β-lactams. As it is shown in Scheme 8 and Table 5, azetidinones **20ca–eg** were successfully reacted with 1 equiv of TBAF affording the corresponding α-methylaryl substituted rings **23**. All the reactions proceeded with good yields of purified products. A very high



Scheme 6.

Table 3. Silylcarbocyclisation reactions of propargyl tosyl amides **8** with aryldimethylsilanes **9**[a]

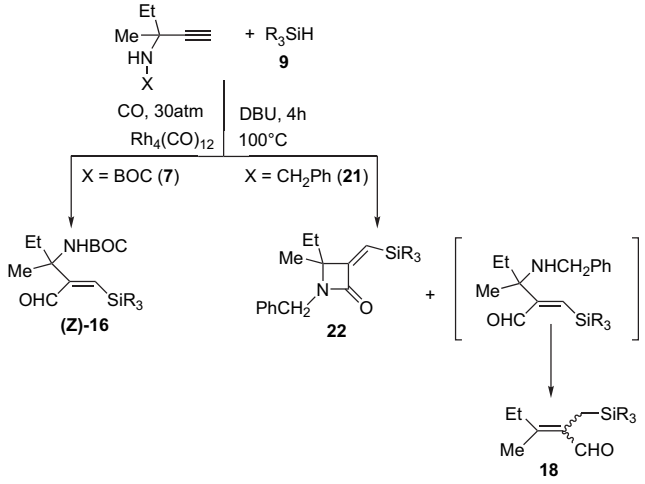
Entry	8	R^1	R^2	9	Ar–	*t* (h)	Conv.[b] (%)	**20**, (*Z*)-**17**	Yield[c] (%)	
									20	(*Z*)-**17**
1	**b**	H	^{t}Bu	**a**	Ph	4	54	**ba**	—	100
2	**b**	H	^{t}Bu	**d**	*p*-Ph–C_6H_4–	4	50	**bd**	—	100 (33)
3	**b**	H	^{t}Bu	**b**	*o*-Me–C_6H_4–	4	59	**bb**	70 (35)	30
4	**c**	Me	Me	**a**	Ph	4	100	**ca**	95 (69)	5
5	**d**	Me	Et	**a**	Ph	4	100	**da**	96 (58)	4
6	**e**	Me	^{t}Bu	**a**	Ph	4	100	**ea**	100 (76)	—
7	**e**	Me	^{t}Bu	**e**	*p*-Me–C_6H_4–	6	58	**ee**	100 (52)	—
8	**e**	Me	^{t}Bu	**f**	*p*-NMe_2–C_6H_4–	6	67	**ef**	100 (45)	—
9	**e**	Me	^{t}Bu	**g**		6	77	**eg**	100 (60)	—

[a] Reactions were performed with 2 mmol of silane, 2 mmol of amide, 2×10^{-3} mmol of $Rh_4(CO)_{12}$, 0.2 mmol of DBU, 3 mL of CH_2Cl_2 in a stainless steel autoclave under 30 atm of CO at 100 °C.
[b] Determined by GLC conversion of silane.
[c] The isolated yields of pure compounds are reported in parentheses.

Table 4. Silylcarbocyclisation reactions of 3-amino-3-methyl-1-pentyne derivatives with arylsilanes[a]

Entry	Substrate		9	R_3	Conv.[b] (%)	Product distribution[c] (%)	
		X					
1	**7**	Boc	**9a**	Me_2Ph	100	—	(*Z*)-**16** (95)
2	**21**	CH_2Ph	**9a**	Me_2Ph	84	**22a** (30)	**18da** (70)
3[d]	**21**	CH_2Ph	**9a**	Me_2Ph	0	—	—
4	**21**	CH_2Ph	**9h**	$MePh_2$	62	**22h** (54)	**18dh** (46)
5	**21**	CH_2Ph	**9i**	Ph_3	0	—	—
6	**21**	CH_2Ph	**9b**	$Me_2(o\text{-}Me\text{-}C_6H_4)$	0	—	—

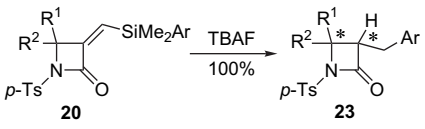
[a] Reactions were performed with 2 mmol of silane, 2 mmol of amine derivative, 2×10^{-3} mmol of $Rh_4(CO)_{12}$, 0.2 mmol of DBU, 3 mL of CH_2Cl_2 in a stainless steel autoclave under 30 atm of CO at 100 °C.
[b] Determined by GLC conversion of silane.
[c] Determined by GLC and ^1H NMR analysis; the percentage of the different products is reported in parentheses.
[d] Reaction performed with 1 equiv of DBU (2 mmol).



Scheme 7.

diastereoselectivity towards the formation of the less hindered (*E*)-β-lactams was observed in all cases regardless of the steric requirements of the silyl moiety of the employed substrates (Table 5, entries 2–6). The configuration of the substituents on the β-lactam rings was confirmed by means of the NOESY spectra. For instance in the cases of 4-*tert*-butyl-1-azetidin-2-ones **23ea–eg**, relevant NOE effects between the *tert*-butyl protons and the adjacent C*H*(CH_2Ar) hydrogen were detected in the (*E*)-products (i.e., *tert*-butyl and CH are in a cis configuration) (Fig. 1).

It is noteworthy that both the functionalised benzene rings and the heteroaromatic thiophenyl ring were transferred from the silicon to the carbon atom with total retention of the initial configuration. All the observed results seemed to indicate that the formation of the arylmethyl-β-lactams is achieved through a reaction pathway very similar to the one proposed for the desilylation reaction of β-silylalkenals.[11] As shown in Scheme 9 a plausible mechanism involves the addition of fluoride to silicon yielding a pentavalent Si atom (**24**), aryl-1,2-anionotropic rearrangement to the adjacent carbon atom with formation of enolate **25**, its possible Brook rearrangement (**26**, **27**)[19] or direct protonation (**28**) and final removal of silyl moiety by water or excess fluoride itself.



Scheme 8.

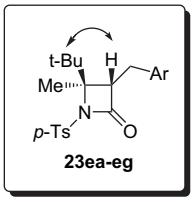
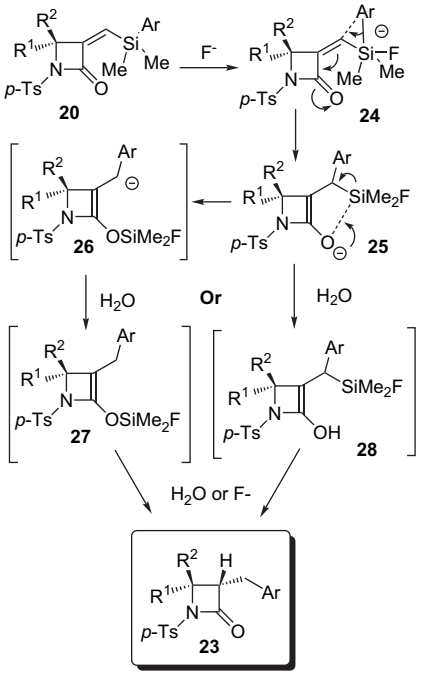


Figure 1.

Table 5. TBAF mediated aryl migration–desilylation reactions of *p*-Ts-β-lactams **20**[a]

Entry	**20**	R^1	R^2	Ar	**23**	Yield[b] (%)	Diastereoselectivity[c]
1	**ca**	Me	Me	Ph	**ca**	60	—
2	**da**	Me	Et	Ph	**da**	58	91/9 (*E*/*Z*)
3	**ea**	Me	^{t}Bu	Ph	**ea**	91	95/5 (*E*/*Z*)
4	**ee**	Me	^{t}Bu	*p*-CH_3–C_6H_4–	**ee**	82	100 (*E*)
5	**ef**	Me	^{t}Bu	*p*-NMe_2–C_6H_4–	**ef**	51	100 (*E*)
6	**eg**	Me	^{t}Bu		**eg**	63	100 (*E*)

[a] Reactions were performed by adding 1 mmol of *p*-Ts-β-lactams to a THF solution (10 mL) of TBAF (2.5 mmol) at room temperature; 100% conversion of the precursors was detected by ^1H NMR analyses.
[b] Yields of pure compounds.
[c] Determined by NOESY spectral analyses.



Scheme 9.

3. Conclusions

In conclusion we have shown that it is possible to prepare α,β-unsaturated aldehydes and 3-methylaryl-β-lactams from easily available propargyl amides through a two-step protocol of silylformylation or silylcarbocyclisation–desilylation processes. Reaction trends are strictly influenced by the structural features of the reagents. The substituent on the nitrogen atom markedly affected both carbonylation reactions, β-silylalkenals and α-silylmethylene-β-lactams being formed in the presence of tosyl protected amines. Poorly hindered propargyl amides reacted smoothly with different arylsilanes and the obtained aldehydes were quantitatively converted into the corresponding unsaturated products with complete diastereoselectivity towards the more stable (*E*) isomers. On the other hand, the cyclisation reactions required hindered substrates to occur with high chemoselectivity. The obtained β-silylmethylene-β-lactams are stable and can be submitted to a desilylation process by treatment with TBAF. No ring opening is observed and the aryl moiety is transferred to the adjacent carbon atom with total retention of its configuration thus generating 3-methylaryl azetidinones that represent useful precursors to amino acid derivatives and potential enzyme inhibitors.

4. Experimental section

4.1. General remarks

All solvents were reagent grade materials purified by standard methods. THF was distilled from sodium, CH_2Cl_2 from P_2O_5 and DBU from KOH just before use. All silanes **9** were distilled and stored under inert gas. Noncommercial silanes **9b–g** were prepared from the corresponding Grignard reagents according to the method described by Hiyama and Fujita.[20] Alkynes **1**, **2**, **4** and TBAF solution (1 M in THF) were purchased from Fluka and used without purification. Alkynes **3**, **5** and **6** were prepared from the corresponding commercial propargyl alcohols according to literature methods.[21] $Rh_4(CO)_{12}$ was prepared and purified as previously reported.[22] ^{1}H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded in $CDCl_3$ solution with Me_4Si or $CHCl_3$ as internal standard; δ values are given in parts per million and coupling constants (J) in hertz. The *Z*/*E* configurations were determined by means of NOE experiments. Infrared absorption spectra were recorded as neat films. Mass spectra were obtained with a Perkin–Elmer Q-Mass 910 connected to a Perkin–Elmer 8500 gas chromatograph. GLC analyses were performed with a DB1 capillary column (30 m×0.52 mm, 5 μm) using He as the carrier gas and a flame ionisation detector (FID). Column chromatography was performed on silica gel 60 (230–400 mesh). All products were identified and characterised by spectroscopic and analytical data.

4.1.1. Synthesis of 3-methyl-3-(*N*-*tert*-butoxycarbonylamino)-1-pentyne, 7. To a solution of 2.83 g (29.2 mmol) of 3-amino-3-methyl-1-pentyne in 44 mL of DMF and 10 mL of triethylamine were added 12.75 g (58.4 mmol) of di-*tert*-butyldicarbonate. The mixture was stirred at 50 °C for 30 min and at 25 °C for 24 h. The reaction mixture was hydrolysed with water (50 mL), extracted with Et_2O (3×30 mL) and the organic layers were washed with diluted HCl and with water until neutral pH. The solvent was removed under vacuum and the crude product purified by distillation affording 4.2 g (73% yield) of 3-methyl-3-(*N*-*tert*-butoxycarbonylamino)-1-pentyne (colourless oil); bp 60 °C (0.1 mmHg); ^{1}H NMR δ 0.96 (3H, t, J=7.2 Hz), 1.41 (9H, s), 1.52 (3H, s), 1.60–2.00 (2H, m), 2.72 (1H, s), 4.65 (1H, s); ^{13}C NMR δ 8.6, 26.6, 28.3, 33.5, 51.1, 69.8, 79.4, 86.3, 153.9; IR ν 3288, 2112, 1700, 1488, 1361, 1250, 1161. Anal. Calcd for $C_{11}H_{19}NO_2$: C 66.97, H 9.71, N 7.10; found: C 66.78, H 9.74, N 7.08.

4.1.2. General procedure for the synthesis of *N*-propargyl-*p*-toluenesulfonamides 8.[23] To a solution of the propargylamine[24] in 15% DMF–water (v/v) was added a slight excess of *p*-TsCl in three portions (60%, 30%, 10% of the total, respectively). After the first addition (60%), the reaction mixture was stirred at 50 °C until the pH of the solution had decreased to ca. 3 and was adjusted to pH 8 with 25% aqueous NaOH. This adjustment was followed with a second portion of *p*-TsCl (30%). Within 20 min the pH was again ca. 3 and readjusted to pH 8 with more 25% NaOH. A final portion (10%) of *p*-TsCl was added. After 10 min, the pH 3 solution was again adjusted to pH ca. 9 and stirred for 2 h, during which time the pH remained approximately constant. The reaction mixture was acidified (to pH 3) with 6 N HCl, cooled in ice with stirring and the snow white product crystals filtered, washed and recrystallised from toluene.

4.1.2.1. *N*-(1-Methyl-2-propynyl)-*p*-toluenesulfonamide (8a).[25] The general procedure was followed using 25 mL of 15% DMF–water solution, 8.15 g (0.043 mol) of *p*-TsCl (total amount) and 2.28 g (0.033 mol) of 3-amino-1-butyne. After the usual work up, it gave 5.09 g (69% yield) of *N*-(1-methyl-2-propynyl)-*p*-toluenesulfonamide as white solid; mp 79–81 °C; ^{1}H NMR δ 1.34 (3H, d, J=6.9 Hz), 2.02 (1H, d, J=2.2 Hz), 2.35 (3H, s), 4.02–4.18 (1H, m),

5.27 (1H, d, J=8.4 Hz), 7.23 (2H, d, J=8.1 Hz), 7.73 (2H, d, J=8.1 Hz); ^{13}C NMR δ 21.4, 23.1, 40.4, 71.7, 82.7, 127.3, 129.4, 137.2, 143.4; MS (EI) m/z (rel int.%): 208 (M^+-15, 24), 155 (40), 132 (5), 91 (100), 77 (5), 68 (7), 65 (20); IR ν 3265, 2110, 1599, 1330, 1158.

4.1.2.2. *N*-(1-*tert*-Butyl-2-propynyl)-*p*-toluenesulfonamide (8b). The general procedure was followed using 10 mL of 15% DMF–water solution, 4.50 g (0.024 mol) of *p*-TsCl (total amount) and 2.22 g (0.020 mol) of 3-amino-4,4-dimethyl-1-pentyne. After the usual work up, it gave 4.12 g (78% yield) of *N*-(1-*tert*-butyl-2-propynyl)-*p*-toluenesulfonamide as white solid; mp 149–153 °C; ^{1}H NMR δ 0.99 (9H, s), 1.99 (1H, d, J=2.4 Hz), 2.42 (3H, s), 3.72 (1H, dd, J=10.2, 2.4 Hz), 5.01 (1H, d, J=10.2 Hz), 7.29 (2H, d, J=8.1 Hz), 7.80 (2H, d, J=8.1 Hz); ^{13}C NMR δ 21.5, 25.7, 35.3, 55.3, 73.2, 80.6, 127.4, 129.4, 137.2, 143.3; MS (EI) m/z (rel int.%): 208 (M^+-57, 15), 155 (34), 139 (18), 110 (23), 91 (96), 65 (36), 54 (100), 41 (10); IR (KBr) ν 3291, 3250, 2116, 1598, 1329, 1162. Anal. Calcd for $C_{14}H_{18}NO_2S$: C 63.61, H 6.86, N 5.30; found: C 63.73, H 6.84, N 5.29.

4.1.2.3. *N*-(1,1-Dimethyl-2-propynyl)-*p*-toluenesulfonamide (8c).[14] The general procedure was followed using 50 mL of 15% DMF–water solution, 19.06 g (0.1 mol) of *p*-TsCl (total amount) and 7.27 g (0.087 mol) of 3-amino-3-methyl-1-butyne. After the usual work up, it gave 10.31 g (50% yield) of *N*-(1,1-dimethylpropynyl)-*p*-toluenesulfonamide as white solid; mp 118–121 °C; ^{1}H NMR δ 1.55 (6H, s), 2.09 (1H, s), 2.42 (3H, s), 4.86 (1H, br s), 7.28 (2H, d, J=8.4 Hz), 7.82 (2H, d, J=8.4 Hz); ^{13}C NMR δ 21.5, 30.7, 49.9, 71.2, 85.5, 127.6, 129.2, 138.9, 143.1; MS (EI) m/z (rel int.%): 222 (M^+-15, 65), 155 (81), 105 (3), 91 (100), 77 (4), 65 (16), 52 (4); IR (KBr) ν 3270, 3232, 2110, 1322, 1149.

4.1.2.4. *N*-(1-Methyl-1-ethyl-2-propynyl)-*p*-toluenesulfonamide (8d).[12] The general procedure was followed using 30 mL of 15% DMF–water solution, 11.4 g (0.060 mol) of *p*-TsCl (total amount) and 5.06 g (0.052 mol) of 3-amino-3-methyl-1-pentyne. After the usual work up, it gave 10.04 g (77% yield) of *N*-(1-methyl-1-ethyl-2-propynyl)-*p*-toluenesulfonamide as white solid; mp 92 °C; ^{1}H NMR δ 0.97 (3H, t, J=7.4 Hz), 1.50 (3H, s), 1.62–1.90 (2H, m), 2.09 (1H, s), 2.41 (3H, s), 5.60 (1H, br s), 7.26 (2H, d, J=8.4 Hz), 7.84 (2H, d, J=8.4 Hz); ^{13}C NMR δ 8.4, 21.4, 27.5, 35.9, 53.9, 72.5, 84.0, 127.5, 129.1, 139.2, 142.8; MS (EI) m/z (rel int.%): 222 (M^+-29, 33), 155 (52), 91 (100), 89 (6), 77 (4), 65 (13); IR (KBr) ν 3290, 2113, 1596, 1321, 1145.

4.1.2.5. *N*-(1-*tert*-Butyl-1-methyl-2-propynyl)-*p*-toluenesulfonamide (8e). The general procedure was followed using 30 mL of 15% DMF–water solution, 14.45 g (0.076 mol) of *p*-TsCl (total amount) and 6.39 g (0.051 mol) of 3-amino-3,4,4-trimethyl-1-pentyne. After the usual work up, it gave 5.69 g (40% yield) of *N*-(1-*tert*-butyl-1-methyl-2-propynyl)-*p*-toluenesulfonamide as white solid; mp 125–127 °C; ^{1}H NMR δ 0.99 (9H, s), 1.45 (3H, s), 2.09 (1H, s), 2.39 (3H, s), 5.21 (1H, br s), 7.24 (2H, d, J=8.4 Hz), 7.80 (2H, d, J=8.4 Hz); ^{13}C NMR δ 21.4, 22.4, 24.8, 38.8, 59.8, 73.5, 83.3, 127.7, 129.0, 138.9, 142.87; MS (EI) m/z (rel int.%): 222 (M^+-57, 46), 155 (63), 139 (5), 108 (3), 91 (100), 77 (5), 68 (22), 57 (7); IR (KBr) ν 3302, 3256, 2124, 1597, 1321, 1157. Anal. Calcd for $C_{15}H_{20}NO_2S$: C 64.72, H 7.24, N 5.03; found: C 6.83, H 7.22, N 5.04.

4.1.3. General procedure for the silylformylation of propargyl derivatives with aryldimethylsilanes catalysed by $Rh_4(CO)_{12}$. Catalytic runs were performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, freshly distilled CH_2Cl_2 (3 mL), previously degassed $ArMe_2SiH$ (2 mmol), the required propargyl derivative (2 mmol) and 2×10^{-3} mmol of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex 'Schlenk' tube. This solution was introduced in the autoclave, previously placed under vacuum (0.1 mmHg), by a steel syphon. The reactor was pressurised with 30 atm of carbon monoxide and the mixture was stirred at 100 °C for 24 h. After removal of excess CO (fume hood), the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through Celite and concentrated in vacuo. The reagent conversion and the product composition were determined by GLC and ^{1}H NMR. The purification of the crude oil by column chromatography on silica gel afforded the pure β-silylalkenals.

4.1.3.1. (*Z*)-2-(Hydroxymethyl)-3-[(dimethylphenyl)-silyl]acrylaldehyde, (*Z*)-11. The crude oil was purified by column chromatography on silica gel using hexane–AcOEt=90/10 as eluent (71% yield, colourless oil); ^{1}H NMR δ 0.52 (6H, s), 2.00 (1H, s), 4.35 (2H, d, J=1.4 Hz), 7.17 (1H, t, J=1.4 Hz), 7.34–7.38 (3H, m), 7.49–7.53 (2H, m), 9.78 (1H, s); ^{13}C NMR δ −0.2, 64.7, 128.8, 130.2, 134.1, 137.8, 140.5, 144.8, 193.8; IR ν 3422, 3066, 2955, 2888, 2700, 1950, 1885, 1811, 1677, 1422, 1250. Anal. Calcd for $C_{12}H_{16}O_2Si$: C 65.41, H 7.32, found: C 65.24, H 7.30.

4.1.3.2. (*Z*)-3-Formyl-4-(dimethylphenylsilyl)-but-3-en-2-yl benzoate, (*Z*)-14. The crude oil was purified by column chromatography on silica gel using hexane–AcOEt=90/10 as eluent (54% yield, colourless oil); ^{1}H NMR δ 0.55 (6H, s), 1.52 (3H, d, J=6.4 Hz), 6.00 (1H, q, J=6.4 Hz), 7.24 (1H, s), 7.38–7.60 (8H, m), 8.04–8.12 (2H, m), 9.85 (1H, s); ^{13}C NMR δ −0.3, 20.5, 68.6, 128.2, 128.4, 129.5, 129.6, 130.2, 133.0, 133.5, 137.3, 147.2, 156.0, 165.2, 191.3; MS (EI) m/z (rel int.%): 323 (11), 261 (11), 217 (100), 218 (19), 181 (6), 139 (15), 105 (69). Anal. Calcd for $C_{19}H_{20}O_3Si$: C 70.34, H 6.21; found: C, 70.55, H 6.23.

4.1.3.3. (*Z*)-3-Acetoxy-3-methyl-2-[(dimethylphenylsilyl)methylene]pentanal, (*Z*)-15.[12] The crude oil was purified by column chromatography on silica gel using hexane–AcOEt=80/20 as eluent (75% yield, colourless oil); ^{1}H NMR δ 0.62 (6H, s), 1.15 (3H, t, J=7.5 Hz), 1.78 (3H, s), 1.96–2.08 (2H, m), 2.13 (3H, s), 6.99 (1H, s), 7.47–7.50 (3H, m), 7.62–7.80 (2H, m), 9.88 (1H, s).

4.1.3.4. (*Z*)-3-Methyl-2-[(dimethylphenylsilyl)methylene]-3-(*tert*-butoxycarbonylamino)pentanal, (*Z*)-16.[12] The crude product was purified by column chromatography on silica gel with dichloromethane (63% yield, colourless

oil); ^{1}H NMR δ 0.62 (6H, s), 0.76 (3H, t, J=7.4 Hz), 1.36 (9H, s), 1.42 (3H, s), 1.66–1.88 (2H, m), 6.91 (1H, s), 7.29–7.54 (5H, m), 9.75 (1H, s); ^{13}C NMR δ −0.4, 7.9, 23.7, 28.2, 31.7, 58.3, 79.0, 127.9, 129.2, 133.5, 138.0, 147.7, 154.3, 157.8, 192.5; IR ν 3354, 2972, 2742, 1718, 1694, 1583, 1426, 1250.

4.1.3.5. (*Z*)-2-[(Dimethylphenylsilyl)methylene]-3-(*p*-tosylamino)butanal, (*Z*)-17aa. The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (71% yield, colourless oil); ^{1}H NMR δ 0.35 (3H, s), 0.36 (3H, s), 1.23 (3H d, J=7 Hz), 2.37 (3H, s), 4.15–4.23 (1H, dq, J=7, 9 Hz), 5.39 (1H, d, J=9 Hz), 6.91 (1H, s), 7.19 (2H, d, J=8.4 Hz), 7.32–7.36 (5H, m), 7.64 (2H, d, J=8.4 Hz), 9.45 (1H, s); ^{13}C NMR δ −0.6, 21.5, 22.3, 53.0, 127.1, 128.2, 129.6, 129.7, 133.4, 136.8, 137.8, 143.2, 150.8, 155.1, 192.3; MS (EI) *m*/*z* (rel int.%): 372 (M^+−15, 15), 292 (10), 281 (27), 230 (29), 215 (25), 198 (9), 155 (52), 141 (13), 135 (55), 105 (12), 91 (100), 77 (8); IR ν 3310, 2965, 2717, 1677, 1596, 1419, 1333, 1250, 1165. Anal. Calcd for $C_{20}H_{25}NO_3SSi$: C 61.98, H 6.50, N 3.61; found: C 61.78, H 6.49, N 3.62.

4.1.3.6. (*Z*)-4,4-Dimethyl-2-[(dimethylphenylsilyl)-methylene]-3-(*p*-tosylamino)pentanal, (*Z*)-17ba. The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (49% yield, colourless oil); ^{1}H NMR δ 0.30 (3H, s), 0.31 (3H, s), 0.83 (9H, s), 2.36 (3H, s), 3.92 (1H, d, J=10.0 Hz), 5.80 (1H, br s), 6.72 (1H, s), 7.16 (2H, d, J=8.4 Hz), 7.30–7.36 (5H, m), 7.58 (2H, d, J=8.4 Hz), 9.36 (1H, s); MS (EI) *m*/*z* (rel int.%): 344 (M^+−85, 19), 228 (100), 189 (69), 174 (27), 149 (37), 135 (19), 91 (57), 77 (3); IR ν 3277, 2962, 2734, 1687, 1597, 1426, 1322, 1247, 1166.

4.1.3.7. (*Z*)-3-Methyl-2-[(dimethylphenylsilyl)methylene]-3-(*p*-tosylamino)butanal, (*Z*)-17ca. The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (42% yield, colourless oil); ^{1}H NMR δ 0.37 (6H, s), 1.44 (6H, s), 2.37 (3H, s), 5.81 (1H, s), 6.93 (1H, s), 7.17 (2H, d, J=8.3 Hz), 7.36–7.41 (5H, m), 7.60 (2H, d, J=8.3 Hz), 9.45 (1H, s); ^{13}C NMR δ −0.4, 21.5, 28.2, 58.0, 127.5, 128.2, 129.4, 129.7, 133.4, 137.0, 138.9, 143.0, 149.7, 157.6, 193.2; MS (EI) *m*/*z* (rel int.%): 306 (M^+−95, 17), 230 (42), 228 (22), 215 (23), 212 (76), 155 (69), 153 (15), 149 (24), 135 (36), 91 (100). Anal. Calcd for $C_{21}H_{27}NO_3SSi$: C 62.81, H 6.78, N 3.49; found: C 62.96, H 6.80, N 3.48.

4.1.3.8. (*Z*)-3-Methyl-2-[(dimethylphenylsilyl)methylene]-3-(*p*-tosylamino)pentanal, (*Z*)-17da. The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (44% yield, colourless oil); ^{1}H NMR δ 0.48 (6H, s), 0.80 (3H, t, J=7 Hz), 1.51 (3H, s), 1.68–1.99 (2H, m), 2.47 (3H, s), 5.88 (1H, s), 6.98 (1H, s), 7.27 (2H, d, J=8.2 Hz), 7.45–7.52 (5H, m), 7.71 (2H, d, J=8.2 Hz), 9.54 (1H, s); ^{13}C NMR δ −0.5, −0.4, 8.1, 21.4, 22.1, 33.9, 61.5, 127.4, 128.2, 129.3, 129.6, 133.4, 137.1, 139.1, 142.9, 151.3, 156.4, 193.1; MS (EI) *m*/*z* (rel int.%): 306 (M^+−95, 17), 230 (42), 228 (22), 215 (23), 212 (76), 155 (69), 153 (15), 149 (24), 135 (36), 91 (100). Anal. Calcd for $C_{22}H_{29}NO_3SSi$: C 63.58, H 7.03, N 3.37; found: C 63.45, H 7.01, N 3.36.

4.1.3.9. (*Z*)-3,4,4-Trimethyl-2-[(dimethylphenylsilyl)-methylene]-3-(*p*-tosylamino)pentanal, (*Z*)-17ea. The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (15% yield, colourless oil); ^{1}H NMR δ 0.40 (6H, s), 0.86 (9H, s), 1.38 (3H, s), 2.35 (3H, s), 6.56 (1H, br s), 6.85 (1H, s), 7.10–7.25 (7H, m), 7.64 (2H, d, J=8.4 Hz), 9.62 (1H, s). Anal. Calcd for $C_{24}H_{33}NO_3SSi$: C 64.97, H 7.50, N 3.16; found: C 65.12, H 7.52, N 3.15.

4.1.3.10. (*Z*)-2-[(Dimethyl-*o*-tolylsilyl)methylene]-3-(*p*-tosylamino)butanal, (*Z*)-17ab. The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (38% yield, colourless oil); ^{1}H NMR δ 0.37 (6H, s), 1.19 (3H, d, J=4.4 Hz), 2.24 (3H, s), 2.36 (3H, s), 4.17 (1H, m), 5.17 (1H, d, J=5.8 Hz), 6.98 (1H, s), 7.10–7.34 (6H, m), 7.60 (2H, d, J=5.2 Hz), 9.36 (1H, s); ^{13}C NMR δ 0.2, 1.3, 21.7, 22.5, 23.6, 52.4, 125.7, 127.3, 129.9, 130.4, 130.5, 134.3, 135.7, 138.0, 143.4, 143.5, 151.8, 155.2, 192.6. Anal. Calcd for $C_{21}H_{27}NO_3SSi$: C 62.81, H 6.78, N 3.49; found: C 62.94, H 6.76, N 3.48.

4.1.3.11. (*Z*)-3-Methyl-2-[(dimethyl-4-methoxyphenylsilyl)methylene]-3-(*p*-tosylamino)butanal, (*Z*)-17cc. The crude oil was purified by column chromatography on silica gel using CH_2Cl_2 as eluent (48% yield, colourless oil); ^{1}H NMR δ 0.39 (6H, s), 1.46 (6H, s), 2.40 (6H, s), 3.82 (3H, s), 5.89 (1H, br s), 6.93 (2H, d, J=7.8 Hz), 6.96 (1H, s), 7.21 (2H, d, J=7.8 Hz), 7.38 (2H, d, J=7.8 Hz), 7.64 (2H, d, J=7.8 Hz), 9.50 (1H, s). Anal. Calcd for $C_{22}H_{29}NO_4SSi$: C 61.22, H 6.77, N 3.25; found: C 61.33, H 6.78, N 3.26.

4.1.4. General procedures for the TBAF promoted rearrangements of (*Z*)-14, (*Z*)-15 and (*Z*)-17. To a solution of 2 mmol of β-silylalkenal in 10 mL of THF were added, at room temperature, 2 mL of TBAF (1 M in THF). The reaction mixture was hydrolysed with water (15 mL), extracted with Et_2O (3×10 mL) and the organic layers were dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent.

4.1.4.1. (*E*)-2-Benzylbut-2-enal, (*E*)-19aa. Yield 52% (colourless oil); ^{1}H NMR δ 2.11 (3H, d, J=7.2 Hz), 3.71 (2H, s), 6.79 (1H, q, J=7.2 Hz), 7.22–7.36 (5H, m), 9.53 (1H, s); ^{13}C NMR δ 15.1, 29.3, 126.0, 128.2, 128.3, 138.9, 143.5, 150.9, 194.4; MS (EI) *m*/*z* (rel int.%): 160 (M^+, 82), 159 (35), 145 (100), 131 (35), 130 (45), 115 (49), 91 (88), 77 (5), 65 (24), 51 (24), 39 (22); IR ν 3023, 2924, 2718, 1682. Anal. Calcd for $C_{11}H_{12}O$: C 82.46, H 7.55; found: C 82.76, H 7.58.

4.1.4.2. (*E*)-2-Benzyl-4,4-dimethylpenten-2-al, (*E*)-19ba.[12] Yield 45% (colourless oil); ^{1}H NMR δ 1.20 (9H, s), 3.80 (2H, s), 6.58 (1H, s), 7.10–7.35 (5H, m), 9.41 (1H, s); ^{13}C NMR δ 26.4, 29.5, 30.1, 125.9, 127.9, 128.3, 139.2, 139.3, 166.0, 196.4; MS (EI) *m*/*z* (rel int.%): 202 (M^+, 36), 187 (8), 159 (40), 145 (32), 131 (53), 115 (37), 91 (85), 77 (8), 65 (16), 55 (23), 51 (30), 43 (40), 41 (100), 39 (89); IR ν 3025, 2959, 2708, 1685, 1632.

4.1.4.3. 2-Benzyl-3-methylbut-2-enal, 19ca. Yield 75% (colourless oil); ^{1}H NMR δ 2.09 (3H, s), 2.34 (3H, s), 3.77

(2H, s), 7.20–7.37 (5H, m), 10.32 (1H, s); ^{13}C NMR δ 19.4, 23.8, 30.7, 125.7, 128.1, 128.2, 135.9, 140.0, 156.7, 190.5; MS (EI) *m*/*z* (rel int.%): 174 (M^+, 93), 159 (100), 131 (31), 129 (24), 128 (24), 115 (27), 91 (73), 68 (25), 51 (20); IR ν 2921, 2756, 1663, 1626. Anal. Calcd for $C_{12}H_{14}O$: C 82.72, H 8.10; found: C 82.70, H 8.08.

4.1.4.4. (*E*)-2-Benzyl-3-methylpenten-2-al, (*E*)-19da.[12] ^{1}H NMR δ 1.08 (3H, *J*=7.8 Hz), 2.31 (3H, s), 2.41 (2H, q, *J*=7.8 Hz), 3.75 (2H, s), 7.19–7.35 (5H, m), 10.31 (1H, s); ^{13}C NMR δ 11.6, 16.7, 30.1, 30.3, 125.7, 128.0, 128.2, 135.0, 140.3, 161.5, 191.3; MS (EI) *m*/*z* (rel int.%): 188 (M^+, 43), 173 (5), 159 (77), 141 (13), 131 (42), 129 (28), 115 (33), 105 (18), 91 (91), 77 (19), 65 (27), 51 (44), 43 (44), 41 (88), 39 (100).

4.1.4.5. (*Z*)-2-Benzyl-3-methylpenten-2-al, (*Z*)-19da.[12] ^{1}H NMR δ 1.26 (3H, t, *J*=7.6 Hz), 2.07 (3H, s), 2.74 (2H, q, *J*=7.6 Hz), 3.73 (2H, s), 7.19–7.35 (5H, m), 10.28 (1H, s); ^{13}C NMR δ 14.2, 21.5, 26.2, 30.7, 125.7, 128.0, 128.2, 135.3, 139.9, 162.6, 190.2; MS (EI) *m*/*z* (rel int.%): 188 (M^+, 48), 159 (74), 141 (13), 131 (42), 129 (26), 128 (26), 117 (26), 115 (31), 105 (17), 91 (89), 77 (19), 67 (26), 65 (27), 53 (25), 51 (44), 46 (45), 41 (40), 39 (100); IR ν 3021, 2965, 2756, 1660, 1616.

4.1.4.6. (*E*)-2-(2-Methylbenzyl)but-2-enal, (*E*)-19ab. Yield 67% (colourless oil); ^{1}H NMR δ 1.90 (3H, d, *J*=7.5 Hz), 2.31 (3H, s), 3.55 (2H, s), 6.80 (1H, q, *J*=7.5 Hz), 7.03–7.09 (5H, m), 9.46 (1H, s); ^{13}C NMR δ 15.4, 20.0, 26.9, 126.2, 126.3, 127.4, 130.3, 136.5, 136.6, 143.2, 151.8, 194.6. Anal. Calcd for $C_{12}H_{14}O$: C 82.72, H 8.10; found: C 82.70, H 8.08.

4.1.4.7. 2-(4-Methoxy-benzyl)-3-methylbut-2-enal, (*Z*)-19cc. Yield 55% (colourless oil); ^{1}H NMR δ 1.99 (3H, s), 2.31 (3H, s), 3.59 (2H, s), 3.75 (3H, s), 6.77 (2H, d, *J*=7.8 Hz), 6.89 (2H, d, *J*=7.8 Hz), 7.05 (2H, d, *J*=7.8 Hz), 7.24 (2H, d, *J*=7.8 Hz), 10.20 (1H, s); ^{13}C NMR δ 19.4, 28.9, 29.8, 55.1, 113.6, 129.3, 132.0, 135.3, 136.2, 157.6, 190.6. Anal. Calcd for $C_{12}H_{14}O_2$: C 75.76, H 7.42; found: C 75.45, H 7.38.

4.1.5. General procedure for the synthesis of α-silyl-methylene-β-lactams. Catalytic runs were performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, 2 mmol of *N*-(propargyl)-*p*-toluenesulfonamide, 3 mL of freshly distilled CH_2Cl_2, 2 mmol of $ArMe_2SiH$, 0.2 mmol of DBU and 2×10^{-3} mmol of $Rh_4(CO)_{12}$ were put, via syringe and under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, previously placed under vacuum (0.1 mmHg), by a steel syphon. The reactor was pressurised to 30 atm of CO and stirred at 100 °C for 4 h. The autoclave was then cooled to room temperature and the excess of CO was removed (fume hood). The reaction mixture was diluted with CH_2Cl_2, filtered through silica gel (CH_2Cl_2 as eluent), concentrated under reduced pressure and recrystallised from hexane. The reagent conversion and the product composition were determined by GLC and ^{1}H NMR.

4.1.5.1. (*Z*)-4,4-Dimethyl-2-(dimethylbiphenylsilyl)-3-(*p*-tosylamino)-pentanal, (*Z*)-17bd. Yield 33% (colourless oil); ^{1}H NMR δ 0.34 (6H, s), 0.97 (9H, s), 2.35 (3H, s), 3.98 (1H, m), 5.96 (1H, m), 6.81 (1H, s), 7.15–7.84 (13H, m), 9.40 (1H, s). Anal. Calcd for $C_{29}H_{35}NO_3SSi$: C 68.87, H 6.98, N 2.77; found: C 69.04, H 6.99, N 2.78.

4.1.5.2. (*Z*)-4,4-Dimethyl-2-[(*o*-tolyldimethylsilyl)-methylene]-3-(*p*-tosylamino)-pentanal, (*Z*)-17bb. Yield 15% (colourless oil); ^{1}H NMR δ 0.36 (3H, s), 0.38 (3H, s), 1.00 (9H, s), 2.30 (3H, s), 2.43 (3H, s), 3.73 (1H, d, *J*=10.3 Hz), 5.22 (NH, d, *J*=10.3 Hz), 7.0 (1H, s), 7.12–7.40 (5H, m), 7.65 (2H, d, *J*=8.4 Hz), 7.82 (2H, d, *J*=8.4 Hz), 9.37 (1H, s); ^{13}C NMR δ 0.0, 21.3, 21.4, 25.7, 35.3, 55.2, 125.3, 127.1, 127.4, 129.3, 129.4, 130.0, 130.1, 134.0, 135.1, 137.2, 142.9, 143.3, 192.4. Anal. Calcd for $C_{24}H_{33}NO_3SSi$: C 64.97, H 7.50, N 3.16; found: C 65.09, H 7.48, N 3.15.

4.1.5.3. (*Z*)-4-*tert*-Butyl-3-[(*o*-tolyldimethylsilyl)-methylene]-1-(*p*-tosyl)-1-azetidin-2-one, (*Z*)-20bb. Yield 35% (white solid); mp 99–101 °C; ^{1}H NMR δ 0.49 (3H, s), 0.51 (3H, s), 0.94 (9H, s), 2.30 (3H, s), 2.41 (3H, s), 4.22 (1H, d, *J*=1.4 Hz), 6.31 (1H, d, *J*=1.4 Hz), 7.10–7.24 (4H, m), 7.29 (2H, d, *J*=7.6 Hz), 7.82 (2H, d, *J*=7.6 Hz); ^{13}C NMR δ −1.8, −1.5, 21.6, 22.9, 26.2, 34.4, 74.1, 125.0, 127.4, 129.7, 129.8, 134.0, 134.6, 135.2, 136.2, 139.8, 143.2, 144.7, 150.6, 161.1. Anal. Calcd for $C_{28}H_{31}NO_3SSi$: C 68.67, H 6.38, N 2.86; found: C 68.82, H 6.39, N 2.85.

4.1.5.4. (*Z*)-4,4-Dimethyl-3-[(dimethylphenylsilyl)-methylene]-1-(*p*-tosyl)-1-azetidin-2-one, (*Z*)-20ca. Yield 69% (white solid); mp 98 °C; ^{1}H NMR δ 0.48 (6H, s), 1.54 (6H, s), 2.41 (3H, s), 6.14 (1H, s), 7.28–7.38 (5H, m), 7.50 (2H, m), 7.90 (2H, m); ^{13}C NMR δ −2.4, 21.6, 24.8, 71.6, 127.2, 128.0, 129.4, 129.8, 132.9, 133.6, 137.0, 137.5, 144.8, 158.9; MS (EI) *m*/*z* (rel int.%): 399 (M^+, 1), 385 (6), 323 (5), 244 (19), 229 (9), 213 (3), 187 (7), 155 (27), 135 (81), 105 (14), 91 (100), 75 (7), 65 (16); IR ν 1766, 1597, 1428, 1354, 1244, 1166. Anal. Calcd for $C_{21}H_{25}NO_3SSi$: C 63.12, H 6.31, N 3.51; found: C 62.90, H 6.33, N 3.50.

4.1.5.5. (*Z*)-4-Ethyl-4-methyl-3-[(dimethylphenylsilyl)methylene]-1-(*p*-tosyl)-1-azetidin-2-one, (*Z*)-20da. Yield 58% (white solid); mp 92 °C; ^{1}H NMR δ 0.49 (6H, s), 0.81 (1H, t, *J*=7.3 Hz), 1.54 (3H, s), 1.83 (1H, dq, *J*=21.8, 7.3 Hz), 2.02 (1H, dq, *J*=21.8, 7.3 Hz), 2.43 (3H, s), 6.11 (1H, s), 7.30–7.38 (5H, m), 7.47–7.53 (2H, m), 7.92 (2H, d, *J*=8.3 Hz); ^{13}C NMR δ −2.4, −2.3, 8.6, 21.7, 23.6, 30.3, 75.7, 127.3, 128.0, 129.4, 129.8, 133.1, 133.6, 133.8, 137.4, 144.8, 157.0, 159.2; MS (EI) *m*/*z* (rel int.%): 384 (M^+−29, 1), 279 (73), 217 (43), 201 (65), 188 (26), 173 (35), 155 (6), 143 (48), 142 (39), 135 (95), 115 (41), 105 (100), 91 (42), 83 (76), 75 (96), 59 (15), 43 (12); IR ν 1764, 1596, 1428, 1354, 1250, 1165. Anal. Calcd for $C_{22}H_{27}NO_3SSi$: C 63.89, H 6.58, N 3.39; found C 63.65, H 6.56, N 3.38.

4.1.5.6. (*Z*)-4-Methyl-4-*tert*-butyl-3[(dimethylphenylsilyl)methylene]-1-(*p*-tosyl)-1-azetidin-2-one, (*Z*)-20ea. Yield 76% (white solid); mp 97 °C; ^{1}H NMR δ 0.48 (3H, s), 0.49 (3H, s), 0.98 (9H, s), 1.68 (3H, s), 2.43 (3H, s), 6.18 (1H, s), 7.30–7.36 (5H, m), 7.37–7.53 (2H, m), 7.92

(2H, d, J=8.3 Hz); ^{13}C NMR δ −2.5, −2.3, 19.1, 21.6, 26.4, 27.7, 83.8, 127.5, 127.9, 129.3, 129.6, 133.6, 134.4, 137.4, 144.6, 157.6, 160.6; MS (EI) m/z (rel int.%): 425 (M^+−16, 4), 279 (73), 217 (49), 201 (74), 188 (30), 155 (5), 145 (54), 135 (78), 105 (100), 91 (28), 77 (91), 75 (95), 61 (16), 59 (18), 53 (24); IR ν 1761, 1596, 1427, 1359, 1245, 1168. Anal. Calcd for $C_{24}H_{31}NSO_3Si$: C 65.27, H 7.07, N 3.17; found: C 65.43, H 7.08, N 3.18.

4.1.5.7. (*Z*)-4-Methyl-4-*tert*-butyl-3-[(dimethyl-*p*-tolylsilyl)methylene]-1-(*p*-tosyl)-1-azetidin-2-one, (*Z*)-20ee. Yield 52% (white solid); mp 98–100 °C; ^{1}H NMR δ 0.49 (3H, s), 0.50 (3H, s), 1.01 (9H, s), 1.70 (3H, s), 2.35 (3H, s), 2.45 (3H, s), 6.19 (1H, s), 7.17 (2H, d, J=7.6 Hz), 7.34 (2H, d, J=8.1 Hz), 7.41 (2H, d, J=7.6 Hz), 7.96 (2H, d, J=8.1 Hz); ^{13}C NMR δ −2.4, −2.2, 19.1, 21.4, 21.6, 26.4, 37.7, 83.8, 127.5, 128.8, 129.6, 133.0, 133.6, 134.7, 137.4, 139.3, 144.6, 157.4, 160.6; IR ν 3066, 2967, 1770, 1448, 1357, 1245, 1171. Anal. Calcd for $C_{25}H_{33}NO_3SSi$: C 65.89, H 7.30, N 3.07; found: C 66.07, H 7.31, N 3.06.

4.1.5.8. (*Z*)-4-Methyl-4-*tert*-butyl-3-[(dimethyl-*p*-dimethylaminophenylsilyl)methylene]-1-(*p*-tosyl)-1-azetidin-2-one, (*Z*)-20ef. Yield 45% (white solid); mp 103–105 °C; ^{1}H NMR δ 0.44 (6H, s), 0.97 (9H, s), 1.66 (3H, s), 2.42 (3H, s), 2.94 (6H, s), 6.18 (1H, s), 6.68 (2H, d, J=8.4 Hz), 7.25–7.38 (4H, m), 7.93 (2H, d, J=8.4 Hz); ^{13}C NMR δ −2.3, −2.1, 19.1, 21.6, 26.3, 37.6, 40.1, 83.6, 111.9, 127.5, 129.1, 129.6, 134.7, 135.8, 137.5, 138.9, 144.6, 156.6, 160.7. Anal. Calcd for $C_{26}H_{36}N_2O_3SSi$: C 64.42, H 7.49, N 5.78; found: C 64.53, H 7.50, N 5.80.

4.1.5.9. (*Z*)-4-Methyl-4-*tert*-butyl-3-[(dimethyl-α-thienylsilyl)methylene]-1-(*p*-tosyl)-1-azetidin-2-one, (*Z*)-20eg. Yield 60% (white solid); mp 110 °C; ^{1}H NMR δ 0.54 (3H, s), 0.56 (3H, s), 1.02 (9H, s), 1.71 (3H, s), 2.43 (3H, s), 6.21 (1H, s), 7.17 (1H, dd, J=4.8, 3.2 Hz), 7.30 (1H, dd, J=3.2, 0.6 Hz), 7.33 (2H, d, J=8.4 Hz), 7.59 (1H, dd, J=4.8, 0.6 Hz), 7.95 (2H, d, J=8.4 Hz); ^{13}C NMR δ −1.3, −1.1, 18.9, 21.5, 26.3, 37.6, 83.8, 127.4, 128.2, 129.5, 131.1, 133.5, 135.0, 136.5, 137.2, 144.6, 157.6, 160.4. Anal. Calcd for $C_{22}H_{29}NS_2O_3Si$: C 59.02, H 6.53, N 3.13; found: C 58.88, H 6.55, N 3.12.

4.1.5.10. (*Z*)-1-Benzyl-3-[(dimethylphenylsilyl)methylene]-4-ethyl-4-methyl-1-azetidin-2-one, (*Z*)-22a. Yield 18% (thick oil); ^{1}H NMR δ 0.57 (6H, s), 0.72 (3H, t, J=7.2 Hz), 1.17 (3H, s), 1.55 (2H, q, J=7.2 Hz), 4.40 (2H, 2d, J=15 Hz), 5.78 (1H, s), 7.20–7.70 (10H, m); ^{13}C NMR δ −2.0, −1.9, 8.5, 22.4, 29.2, 43.4, 68.2, 124.2, 127.5, 127.6, 127.8, 128.5, 129.0, 133.7, 136.9, 138.5, 161.5, 163.3; MS (EI) m/z (rel int.%): 349 (M^+, 1), 348 (M^+−H, 1), 334 (M^+−15, 24), 320 (9), 272 (19), 135 (39), 91 (100); IR ν 3064, 2962, 1738, 1455, 1379, 1248, 1113. Anal. Calcd for $C_{22}H_{27}NOSi$: C 75.59, H 7.79, N 4.01; found: C 75.70, H 7.77, N 4.02.

4.1.5.11. (*Z*)-1-Benzyl-3-[(methyldiphenylsilyl)methylene]-4-ethyl-4-methyl-1-azetidin-2-one, (*Z*)-22h. Yield 21% (thick oil); ^{1}H NMR δ 0.09 (3H, s), 0.76 (3H, t, J=7.2 Hz), 1.21 (3H, s), 1.54–1.66 (2H, m), 4.32 (1H, d, J=15.3 Hz), 4.50 (1H, d, J=15.3 Hz), 6.00 (1H, s), 7.20–7.65 (15H, m); ^{13}C NMR δ −3.1, 8.5, 22.6, 29.2, 43.5, 68.4, 121.9, 127.6, 127.8, 128.6, 129.3, 134.6, 134.7, 136.5, 136.9, 162.9, 163.0; MS (EI) m/z (rel int.%): 396 (M^+−15, 1), 334 (21), 197 (25), 137 (8), 105 (13), 91 (100), 77 (3), 53 (8), 43 (10); IR ν 3066, 2968, 1739, 1456, 1252. Anal. Calcd for $C_{27}H_{29}NOSi$: C 78.79, H 7.10, N 3.40; found: C 78.64, H 7.12, N 3.41.

4.1.5.12. (*Z*)-3-Methyl-2-[(dimethylphenylsilyl)methyl]-2-pentenal, (*Z*)-18da. Colourless liquid; ^{1}H NMR δ 0.27 (6H, s), 0.94 (3H, t, J=7.4 Hz), 1.99 (2H, s), 2.03 (2H, q, J=7.4 Hz), 2.13 (3H, s), 7.15–7.62 (5H, m), 10.14 (1H, s); ^{13}C NMR δ −2.5, 14.6, 15.1, 23.3, 29.9, 127.6, 128.0, 128.9, 133.5, 139.0, 156.4, 191.1; MS (EI) m/z (rel int.%): 246 (M^+, 1), 231 (13), 217 (19), 137 (16), 136 (14), 135 (100), 105 (11), 43 (42), 41 (23), 39 (16). Anal. Calcd for $C_{15}H_{22}OSi$: C 73.11, H 9.00; found: C 73.25, H 8.98.

4.1.5.13. (*E*)-3-Methyl-2-[(dimethylphenylsilyl)methyl]-2-pentenal, (*E*)-18da. Colourless liquid; ^{1}H NMR δ 0.28 (6H, s), 1.09 (3H, t, J=7.4 Hz), 1.67 (3H, s), 1.97 (2H, s), 2.55 (2H, q, J=7.4 Hz), 7.15–7.62 (5H, m), 10.10 (1H, s). Anal. Calcd for $C_{15}H_{22}OSi$: C 73.11, H 9.00; found: C 73.23, H 9.01.

4.1.5.14. (*Z*)-3-Methyl-2-[(methyldiphenylsilyl)methyl]-2-pentenal, (*Z*)-18dh. Colourless liquid; ^{1}H NMR δ 0.46 (3H, s), 0.78 (3H, t, J=7.4 Hz), 1.85 (2H, q, J=7.4 Hz), 2.06 (3H, s), 2.30 (2H, s), 7.32–7.56 (10H, m), 10.07 (1H, s); ^{13}C NMR δ −3.6, 13.2, 13.6, 16.3, 29.9, 127.7, 129.7, 133.0, 134.5, 136.9, 157.1, 191.1; MS (EI) m/z (rel int.%): 308 (M^+, 0.3), 307 (M^+−H, 0.4), 279 (9), 231 (10), 197 (100), 181 (8), 165 (7), 137 (26), 119 (9), 105 (23), 93 (10), 53 (18), 43 (29). Anal. Calcd for $C_{20}H_{24}OSi$: C 77.87, H 7.84; found: C 77.97, H 7.82.

4.1.5.15. (*E*)-3-Methyl-2-[(methyldiphenylsilyl)methyl]-2-pentenal, (*E*)-18dh. Colourless liquid; ^{1}H NMR δ 0.48 (3H, s), 0.99 (3H, t, J=7.4 Hz), 1.50 (3H, s), 2.27 (2H, s), 2.48 (2H, q, J=7.4 Hz), 7.32–7.56 (10H, m), 10.03 (1H, s); ^{13}C NMR δ −3.5, 11.1, 14.5, 21.7, 26.1, 127.7, 129.2, 133.4, 134.4, 134.5, 158.3, 190.1. Anal. Calcd for $C_{20}H_{24}OSi$: C 77.87, H 7.84; found C 77.75, H 7.81.

4.1.6. General procedures for the TBAF promoted rearrangements of (*Z*)-20. To a solution of 2 mmol of (*Z*)-**20** in 10 mL of THF was added, at room temperature, 2 mL of TBAF (1 M in THF). The reaction mixture was hydrolysed with water (20 mL), extracted with Et_2O (3×10 mL) and the organic layers were dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel using CH_2Cl_2 as eluent.

4.1.6.1. 3-Benzyl-4,4-dimethyl-1-(*p*-tosyl)-1-azetidin-2-one, 23ca. Yield 60% (thick oil); ^{1}H NMR δ 1.55 (3H, s), 1.62 (3H, s), 2.50 (3H, s), 2.85 (1H, dd, J=15, 9.2 Hz), 3.14 (1H, dd, J=15, 6.6 Hz), 3.33 (1H, dd, J=9.2, 6.6 Hz), 7.18–7.38 (5H, m), 7.40 (2H, d, J=8.4 Hz), 7.97 (2H, d, J=8.4 Hz); ^{13}C NMR δ 21.6, 21.7, 27.3, 30.5, 60.2, 66.9, 126.6, 127.2, 128.2, 128.6, 129.8, 137.2, 137.5, 144.9, 166.2; IR ν 2978, 1782, 1358, 1165. Anal. Calcd for $C_{19}H_{21}NO_3S$: C 66.45, H 6.16, N 4.08; found: C 66.58, H 6.17, N 4.09.

4.1.6.2. (*E*)-3-Benzyl-4-ethyl-4-methyl-1-(*p*-tosyl)-1-azetidin-2-one, (*E*)-23da. Yield 58% (thick oil); ^{1}H NMR δ 0.75 (3H, t, J=7.4 Hz), 1.57 (3H, s), 1.71–1.89 (1H, m), 1.99–2.14 (1H, m), 2.51 (3H, s), 2.79 (1H, dd, J=14.6, 8.6 Hz), 3.14 (1H, dd, J=14.6, 6.6 Hz), 3.32 (1H, dd, J=8.8, 6.6 Hz), 7.20–7.38 (5H, m), 7.40 (2H, d, J=8.0 Hz), 7.99 (2H, d, J=8.0 Hz); ^{13}C NMR δ 8.5, 19.4, 21.5, 30.8, 32.4, 57.7, 70.7, 126.6, 127.2, 128.4, 128.6, 129.7, 137.2, 137.7, 144.8, 166.3; IR ν 2969, 1781, 1357, 1163. Anal. Calcd for $C_{20}H_{23}NO_3S$: C 67.20, H 6.49, N 3.92; found: C 67.06, H 6.47, N 3.91.

4.1.6.3. (*E*)-3-Benzyl-4-*tert*-butyl-4-methyl-1-(*p*-tosyl)-1-azetidin-2-one, (*E*)-23ea. Yield 91% (thick oil); ^{1}H NMR δ 0.98 (9H, s), 1.69 (3H, s), 2.51 (3H, s), 2.75 (1H, dd, J=14.4, 7 Hz), 3.09 (1H, dd, J=14.4, 8.2 Hz), 3.42 (1H, dd, J=8.2, 7 Hz), 7.25–7.35 (5H, m), 7.40 (2H, d, J=8.6 Hz), 8.01 (2H, d, J=8.6 Hz); ^{13}C NMR δ 16.2, 21.6, 25.8, 31.3, 37.0, 55.9, 78.6, 126.7, 127.7, 128.6, 128.8, 129.6, 136.9, 138.0, 144.8, 167.7; IR ν 2958, 1773, 1356, 1167. Anal. Calcd for $C_{22}H_{27}NO_3S$: C 68.54, H 7.06, N 3.63; found: C 68.33, H 7.04, N 3.62.

4.1.6.4. (*E*)-3-(4-Methylbenzyl)-4-*tert*-butyl-4-methyl-1-(*p*-tosyl)-1-azetidin-2-one, (*E*)-23ee. Yield 82% (thick oil); ^{1}H NMR δ 0.93 (9H, s), 1.61 (3H, s), 2.29 (3H, s), 2.43 (3H, s), 2.65 (1H, dd, J=14.2, 6.6 Hz), 2.97 (1H, dd, J=14.2, 8.2 Hz), 3.34 (1H, dd, J=8.2, 6.6 Hz), 7.09 (4H, m), 7.32 (2H, d, J=8.2 Hz), 7.94 (2H, d, J=8.2 Hz); ^{13}C NMR δ 16.1, 20.8, 21.5, 25.6, 30.7, 36.8, 55.9, 78.4, 127.5, 128.6, 129.1, 129.5, 134.8, 136.0, 136.8, 144.7, 167.6; IR ν 2964, 1774, 1379, 1357, 1171. Anal. Calcd for $C_{23}H_{29}NO_3S$: C 69.14, H 7.32, N 3.51; found: C 69.27, H 7.34, N 3.52.

4.1.6.5. (*E*)-3-[4-(Dimethylamino)benzyl]-4-*tert*-butyl-4-methyl-1-(*p*-tosyl)-1-azetidin-2-one, (*E*)-23ef. Yield 51% (thick oil); ^{1}H NMR δ 0.91 (9H, s), 1.60 (3H, s), 2.43 (3H, s), 2.58 (1H, dd, J=14.4, 7.0 Hz), 2.89 (6H, s), 2.96 (1H, dd, J=14.4, 7.0 Hz), 3.26–3.34 (1H, m), 6.63 (2H, d, J=8.8 Hz), 7.05 (2H, d, J=8.8 Hz), 7.32 (2H, d, J=8.3 Hz), 7.93 (2H, d, J=8.3 Hz); ^{13}C NMR δ 16.2, 21.6, 25.8, 30.3, 36.9, 40.6, 56.3, 78.6, 112.8, 125.6, 127.6, 129.4, 129.6, 137.0, 144.7, 149.4, 168.0; IR ν 2960, 1771, 1380, 1354, 1168. Anal. Calcd for $C_{24}H_{32}N_2O_3S$: C 67.26, H 7.53, N 6.54; found: C 69.13, H 7.51, N 6.53.

4.1.6.6. (*E*)-4-*tert*-Butyl-4-methyl-3-[(thiophen-2-yl)-methyl]-1-(*p*-tosyl)-1-azetidin-2-one, (*E*)-23eg. Yield 60% (thick oil); ^{1}H NMR δ 0.93 (9H, s), 1.62 (3H, s), 2.43 (3H, s), 2.95 (1H, dd, J=15.4, 7.4 Hz), 3.18 (1H, J=15.4, 7.4 Hz), 3.37 (1H, t, J=7.4 Hz), 6.67–6.92 (2H, m), 7.10–7.13 (1H, m), 7.33 (2H, d, J=8.3 Hz), 7.93 (2H, d, J=8.3 Hz); ^{13}C NMR δ 16.0, 21.6, 25.4, 25.7, 37.0, 56.1, 78.7, 124.1, 126.1, 127.1, 127.7, 129.6, 136.8, 140.0, 144.9, 167.0; IR ν 2960, 1773, 1380, 1356, 1170. Anal. Calcd for $C_{20}H_{25}NO_3S_2$: C 61.35, H 6.44, N 6.58; found: C 67.44, H 6.48, N 6.60.

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